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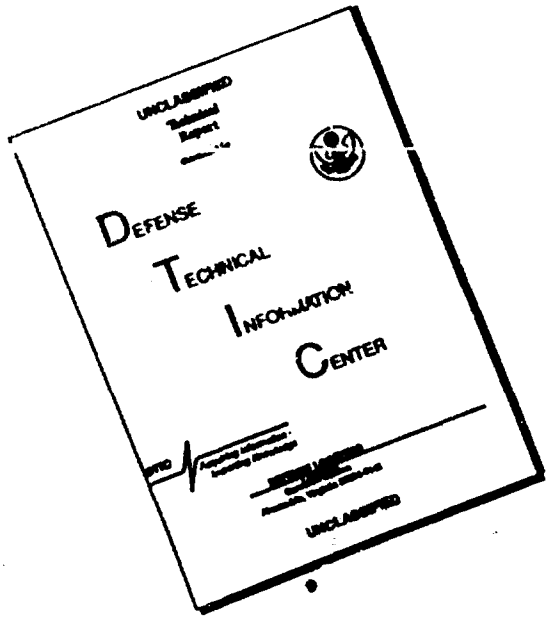

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MATHEMATICAL MODEL OF HYDRATION OF BIOPOLYMERS IN SOLUTION

[Following is the translation of an article by L. G. Sedykh and N. V. Sedykh, Kazan State University imeni V. I. Ulyanova-Lenina, published in the Russian-language periodical Biofizika (Biophysics), Vol XII, No 5, 1967, pages 936-938. It was submitted on 12 Dec 1966.]

The problem of determining the boundaries of hydration of biopolymers in solution depending on pH of the medium, asymmetry of macromolecules, its chemical composition, energies of bonds which are participating in hydration, their quantity, and also the coordination number of molecules of water has been formulated quite accurately with the help of a model of whole number linear programming.

Mathematical Statement of the Problem

It is known that proteins and nucleic acids have n various types of hydrophilic groups.

We will designate the number of hydrophilic groups of the i type ($i = \overline{1,n}$) in a molecule by x_i .

The process of hydration consists of the orientation of hydrophilic groups with an expenditure of a specific energy of a certain number of water molecules, from which is formed the so-called monolayer or more ordered (solidly bound) water.

We will designate the amount of water which is solidly oriented by the i hydrophilic group by c_i , and the energy of this orientation by a_i . Further orientation of water molecules by hydrophilic groups leads to the formation of a certain amount of less ordered (weakly bound) water immediately adjacent to the monolayer.

Since each hydrophilic group orients water with a specific energy then the total energy of all hydrophilic groups on a molecule can be written in the form

$$\sum_{i=1}^{n} A_i x_i \quad .$$

This energy sould not exceed the total energy (A) of the monolayer, that is, the numbers $x_1, x_2 \ldots x_n \ldots$ should satisfy the inequality

$$\sum_{i=1}^{n} A_i x_i < A \qquad (1)$$

Various types of hydrophilic groups are encountered on a molecule through j amino acid radicals. j for different types of hydrophilic groups can be various. Having designated the total number of monomer units in a macromolecule by Z, the number of types of hydrophilic groups which are encountered through j amino acids and no more than one time on the radical by P, and the number of types of hydrophilic groups which are encountered through j radicals more than one time on each of them by P', it is possible to write the inequality

$$\sum_j x_j < P\left(\left[\frac{Z}{j+1}\right]+1\right)+\left[\frac{Z}{20}\right]\cdot P' \qquad (2)$$

Summation is conducted based on those types of hydrophilic groups which are encountered through the same number of amino acid radicals. A unit is added in the event Z is not divided completely by $j+1$.

This inequality usually breaks down into a number of inequalities.

Since each hydrophilic group is encountered on a macromolecule no less than one time and their number cannot be divided, this should fulfill the condition

$$x_i \geqslant 1, \text{ whole.} \qquad (3)$$

As is known, many biopolymers are polyelectrolytes. Therefore, during the solving of concrete problems it is necessary to take into consideration that at neutral pH certain hydrophilic groups, for example, COO^- and NH^+ , disappear, that is, components $x = 0$, and at alkaline and acid pH's again appear.

With a change in form of the molecule some hydrophilic groups may be screened or, conversely, take part in hydration. In the first case components $c_i = 0$ and in the second $c_i = 0$ ($i = 1\overline{n}$).

According to certain data the greatest hydration is observed at $a/b > 1$ and it decreases in the case of $a/b = 1$ [1], where b - width and a - length of the molecule.

Suppose it is necessary to determine the boundaries of a monolayer and less ordered water with a calculation of all the above formulated limitations.

Since each hydrophilic group of the i type solidly orients c_i water molecules, the total amount of water taking part in the formation of the monolayer can be written in a linear form

$$\sum_{i=1}^{n} c_i x_i. \qquad (4)$$

Since we are interested in the boundaries of more ordered water then the problem amounts to finding a vector $x = (x_1, x_2, \ldots, x_n)$, satisfying the limitation (1, 2, 3) and reversing into maximum, for finding the upper limit, and into minimum, for finding the lower limit of the monolayer, the linear form (4)

$$\sum_{i=1}^{n} c_i x_i \rightarrow \max \text{ (min)}. \qquad (5)$$

Making use of the solution found with a calculation of the orientation of water in a monolayer and the coordination number of water molecules, it is not difficult to calculate the boundaries of less ordered water under the same conditions.

The problem set up above is a problem of whole number linear programming and may be solved by the method of Gomory [2] or by the method of dynamic programming [3]. Setting up such a problem for a concrete biopolymer and checking it on an electronic computer (...) with limitations (1, 2, 3), it is possible to determine the number of hydrophilic groups of different types and the number of water molecules taking part in hydration.

In a comparison of calculated data with those obtained experimentally it is possible to make up a more accurate picture of the phenomenon of biopolymer hydration.

Solution of Concrete Problems

A calculation was made of hydration of serum albumin, egg albumin, and cytoplasmic proteins of ...tions 0.2 and 0.7, isolated from plants [4], in a solution.

The results obtained, in a comparison with those known for animal proteins [5-7] and experimentally determined by the method of dielkometriya [Exact translation not established. Ed.] at ultra-high frequency [8, 9] for plant proteins, are presented in the table.

Quantity of Water Molecules per 1 Molecule of Protein

	(a) Упорядоченная вода в монослое				(b) Менее упорядоченная вода			
	(c) минимальное		(d) максимальное		(c) минимальное		(d) максимальное	
	(e) вычисл.	(f) эксперим.	вычисл.	эксперим.	вычисл.	эксперим.	вычисл.	эксперим.
(g) Серуальбумин	220	210	1221	1200	1118	1100	2705	2680
(h) Яичный альбумин	165	150	570	570	565	570	1790	1780
(i) Ф — 0,2	200	180±10	540	550±28	520	—	1200	—
Ф — 0,7	100	110±6	230	210±10	190	—	500	—

Key: (a) Ordered water in monolayer; (b) Less ordered water; (c) Minimum; (d) Maximum; (e) Calculated; (f) Experimental; (g) Serum albumin; (h) Egg albumin; (i) Fraction.

As it follows from the table the boundaries of calculated hydration coincide sufficiently well with those obtained experimentally. Thus the possibility is presented of using the constructed model as a method for calculating the boundaries of hydration of biopolymers. It follows to note that a portion of fixed water enters into the experimentally obtained value of the monolayer, that is, water, the circulation of which in an external ultra-high frequency field is mechanically restrained by a macromolecule. The amount of such water for biopolymers which are striving for maximum hydration can be determined if the calculated amount of water is subtracted from the experimentally obtained value. In a comparison of experimental data with that calculated from the model it is possible to determine how completely the hydrophilic bonds belonging to the macromolecule are replaced by water, that is, to what extent the hydration of protein differs from the maximum possible. In the above cited calculation the presence of more or less ordered water was assumed and the result was the maximum possible amount of hydratable water in protein solutions from 0.3 g/g to 0.[illegible] of protein. This value is supported by various methods of measurement [10]. If it is assumed that polyhydration takes place (several layers of ordered water), then the maximum possible amount of hydratable water increases by 2-3 times, which does not correspond to calculated and experimental data. In connection with this the idea of polyhydration [11] is not confirmed.

It is necessary to note that hydration water is continuously exchanged with moving (free) water, which indicates a change in the times of longitudinal and transverse magnetic relaxation [12]. In connection with this the boundaries of a monolayer and less ordered water, determined both from calculation and from experiment, are averaged out in time.

Conclusions

A mathematical model has been proposed which describes sufficiently well the process of hydration of biopolymers in solution.

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